GRAPHITE AND BN/ALN ANNEALING CAPS FOR
ION IMPLANTED SIC

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ABSTRACT

The activation of dopants for wide band-gap semiconductors such as SiC is a subject of much research.. Silicon Carbide is problematic as Si sublimates from the SiC matrix at the temperatures required for activation. We have investigated the success of capping SiC substrates with more thermally stabile materials to impede Si sublimation. We present data taken from the SiC capping strategies using carbon and AlN/BN surface caps. We found that the C cap protects the surface at all analyzed annealing temperatures. While the nitride cap protects the surface at all temperatures, however, it was very difficult to remove. There were modest increases in the sheet resistance for the C capped material when compared to the nitride capped material with the exception of the graphite capped 1800º sample.

1. INTRODUCTION

Silicon carbide is a wideband-gap material that holds much promise for next generation electronics. The material has relatively good crystallinity a large energy gap and perhaps more importantly excellent thermal stability and conductivity. However, the material has not been fully realized for several reasons. One is that it is difficult to activate dopants within the SiC matrix.

Thermal activation of implants is one of the most common methods of dopant activation. However, the temperature required to activate dopants in SiC is above the sublimation temperature for Si in the SiC matrix. Annealing to these temperatures will lead to a carbon rich surface and loss of SiC characteristics. This process is measurable at 1500ºC and is very problematic at 1600ºC.

Our research group has employed a variety of different surface capping strategies to minimize Si sublimation from the surface. Previously we attempted to utilize graphite as an annealing cap for ion implanted SiC and found that the graphite formed crystallites, and that "blow holes" were produced in the capping layer by Si vapor when annealed to 1700ºC. We also found it more difficult to remove the graphite crystallites with an oxygen plasma than it was to remove the caps annealed at lower temperatures More importantly we found that the sheet resistance was larger than it was for a sample capped with BN/AlN and annealed at the same temperature. (Jones 2002).

We found that the sheet resistance was slightly larger for a C capped material than it was for a sample coated with a BN/AlN cap annealed at the same temperature.

However, the results of Negoro (Negoro 2004) using a C-cap were quite different in that the C did not form crystallites, no blow holes formed at higher annealing temperatures, and the cap was easy to remove with an oxygen plasma. Their methodology employed a different method of C-cap deposition. We have now been able to replicate Negoro's results and in this presentation compare the C-cap and the BN/AlN cap.

All samples were analyzed by SEM, SIMS, XRD, TEM, AFM, RBS, and Hall effect measurements to determine the success of the capping strategy. The synergy of the different characterization methods highlights the importance of analytical measurements in understanding issues of importance to the development of new materials for sensors, and microelectronics for the war fighter.

2. EXPERIMENTAL:

In the present work, a wafer of ,B doped semi-insulating intrinsic silicon carbide was ion implanted with Al to 10^{20} cm^{-3}, using an implant scheme of 30, 70 and 180 keV to produce a box implant with a depth of 0.3 µm. After implantation the sample was cleaved to produce multiple smaller samples. These samples were

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then either coated with photoresist, or coated with nitride.

This was done by implanting an on-axis semi-insulating 4H-SiC wafer with cutting the wafer into smaller pieces, depositing the caps, and annealing them for 30 min at temperatures ranging from 1500 to 1800ºC and examining them using SEM, SIMS, XRD, TEM, AFM, RBS, and Hall effect measurements.

Prior to capping, the substrates were cleaned, the AlN and BN films were grown by PLD as described earlier (Ruppalt 2003), and a uniform C-cap layer was formed by depositing and spinning photoresist as is described in our earlier work (Gao 2001). Afterward, the photoresist film was baked at 225ºC for 10 min and annealed for 10 min at 750ºC in argon ambient. The samples were annealed in pairs at 1500, 1600, 1650, 1700, and 1800ºC in an RF heated furnace.

After the caps had been examined for blow holes and/or evaporation pits, the samples were examined by SIMS and SEM before removing the caps and examining the the SiC surfaces. The BN cap was ion milled off, the AlN cap was etched off in warm (80ºC) KOH, and the C-caps were removed by burning them off in an oxygen ambient for 1 hr at 800ºC.

The samples were then all analyzed by a suite of chemical, structural, and electronic assessment tools. Scanning electron microscopy was utilized to visually access the sample surface. Secondary ion mass spectrometry (SIMS) was utilized to access the stability of the capping strategy and the mobility of the dopant as a function of annealing temperature. The technique of X-Ray Diffraction (XRD) was utilized to evaluate the crystallinity of the material. Transmission electron microscopy (TEM) was employed to examine the structural differences and examine dislocations within the material. Atomic force microscopy (AFM) was utilized to evaluate the surface of the annealed cap and the surface structure of the SiC after removing the capping layer. Rutherford Backscattering spectroscopy (RBS) was utilized to determine implant depth and cross check experimental results. Hall effect measurements were used to determine the electrical properties of the resultant materials.

3. RESULTS

The first line of examination of the samples was comparison of images of the samples before and after annealing of both capped surfaces. No significant differences were seen in the micrographs for any of the annealing temperatures.

Previously we had noted "blow holes" in the surface of some caps. These blow holes were presumably the result of sublimation of Si from the SiC matrix creating subsurface pressure—probably collecting in macroscopic defect pockets. There was no evidence of blow holes in either type of cap. Also, the faceted crystallites on the surface of the graphite seen previously for samples annealed at 1700ºC were not present this time. However, there is macroscopic evidence of an uncharacterized surface chemical processes visible at low optical microscope magnification.

Further investigations utilized X-ray diffraction techniques. The crystallinity of the samples annealed at 1600, 1700 or 1800ºC were examined using X-ray θ - 2θ scans. A representative scan is shown is figure 1. The spectra for the nitride coated samples were similar; the BN and AlN films have a strong hexagonal (0001) texture, but a small (10$\underline{1}$0) BN peak was also present.
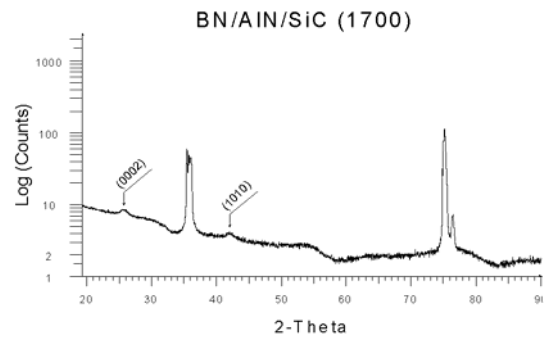
X-Ray Scan for BN/AlN/4H-SiC

Figure 1. AlN has an (0002 texture, but there are other orientations as well)

The scans for the C-coated samples annealed at 1600 and 1700ºC are similar in that they show a strong (0001) graphite peak, but no such peak was found for the sample annealed at 1800ºC even when the step time was doubled (as shown in figure 2). This can be explained by the graphite film being too thin.
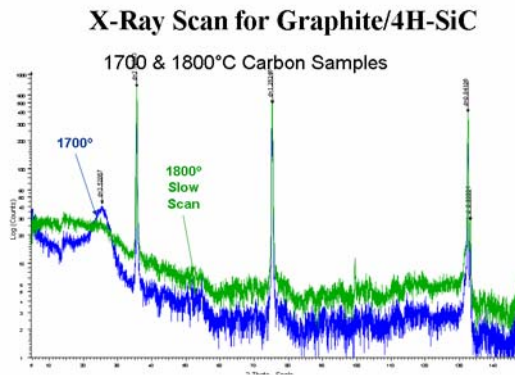
X-Ray Scan for Graphite/4H-SiC

Figure 2: An (0002) peak detected in sample annealed at 1700ºC, but not in the sample annealed at 1800ºC even for a slow scan

This explanation is supported by the data in the SIMS depth profile of the 1800ºC graphite coated sample. This data is shown in figure 3 and highlights that the cap has been reduced to approximately < 20% of the thickness of the others – 200 nm vs. 1300 nm for the other samples. This estimate uses the assumption that the sputter rate is uniform for the annealed and unannealed samples.

It is interesting to note that the apparent sublimation of C can not be accounted for by temperature alone. The vapor pressure of C even at 1800ºC is relatively low.

Silicon SIMS Profiles in C-Cap
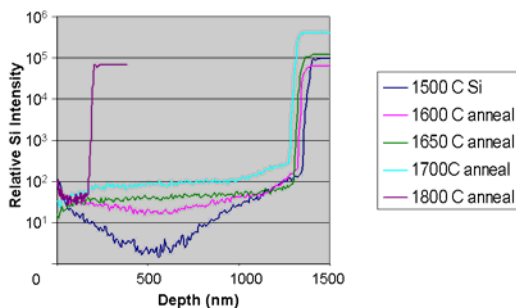
Figure 3: The apparent Si out-diffusion increases with the annealing temperature. Also, the cap for the 1800ºC sample is much thinner. All graphs have been offset to allow for visual comparison.

An alternative explanation is that the Si from the SiC diffuses out, and reacts with the C cap, to form more volatile Si_xC_y species. This may be seen in the SIMS profiles where there is some Si out-diffusion into the C-cap. The Si may aggregate at the surface of the C Cap at 1500ºC because the Si_xC_y species are not volatile.

Whereas, at 1600ºC the pile-up is very small, and at 1650 and 1700ºC the Si concentration drops off at the surface presumably because the Si has escaped through the evaporation of some of the Si_xC_y species.
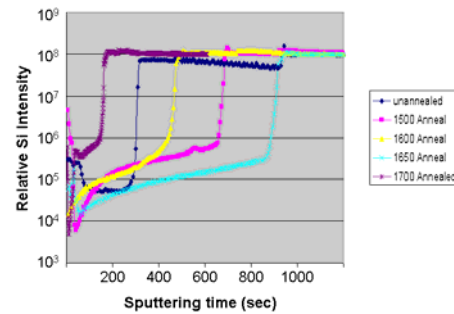
Silicon SIMS Profiles in AlN-Cap

Figure 4: The film thicknesses were the same; the sputtering time was changed to separate the data. Some Si out-diffusion might occur at 1700ºC.

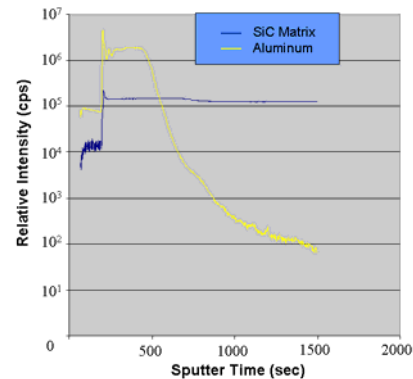## Aluminum SIMS Profile in SiC for C-Capped Sample Annealed at 1800ºC

Figure 5: The integrated aluminum content is almost as large as that of the programmed implant. Little Al diffusion has occurred at 1800ºC as the implant peaks can still be distinguished.

Some of the implanted Al may also be lost through out-diffusion, as there is evidence of Al above base line levels within the C cap. Figure 4 shows the SIMS data from the AlN/BN capping scheme. It is possible that there is a replacement mechanism where the Al replaces the diffused Si from the SiC/graphite interface. However, it should be noted that the implant peaks are clearly visible in the SIMS profile of the box implant, as shown in Figure5, and therefore, large scale diffusion of the Al is not occurring. Obviously it is not possible to profile the Al diffusion through an AlN cap, and the data on Si out-diffusion is obscured as the nitride cap contains Si impurities. That being said, there appears to be a little more Si in the samples annealed at the higher temperatures.

Transmission electron microscopy (TEM) reveals that there is a transition layer between the SiC and the C-cap. This layer is likely due to out-diffusion of Si and can be seen in fig 6.

TEM of C-Capped Sample Annealed at 1800ºC

Figure 6. Low magnification TEM image from the 4H-SiC surface reveals a top layer of thickness ~ 8 nm that has undergone a chemical reaction during the annealing at 1800 ºC.

For the C-coated sample annealed at 1800ºC, it was seen that this layer is ~ 80 nm thick. One can see in the HRTEM shown in figure 7, that the interface between the graphite and the SiC is not sharp, as there are pits in the SiC two to three atomic layers thick that are probably created by the reaction between the graphite and SiC. It can also be seen in the C-capped sample that the graphite has crystallized in a few places, and that its basel plane is aligned with the basal plane of SiC The top five-six unit cells of the SiC surface have decomposed due to chemical reaction at the interface during the annealing at 1800ºC. The 2-3 nm thick layer above the SiC substrate can be identified as the hexagonal phase of graphite (PDF 41-1487) as confirmed with SAD. The (0002) planes of the graphite are seen as nearly parallel to the (0004) planes of the 4H-SiC.

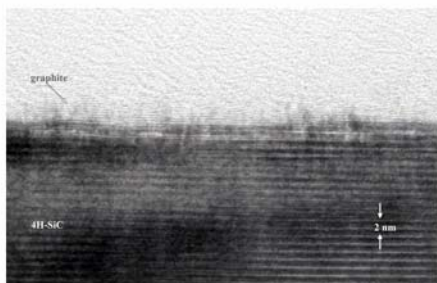**HRTEM of C-Capped Sample Annealed at 1800ºC**

Figure 7: HRTEM from the C/4H-SiC interface.

The interface between the AlN and SiC for the sample annealed at 1700ºC is atomically sharp, as the AlN appears to grow epitaxially on the SiC surface.
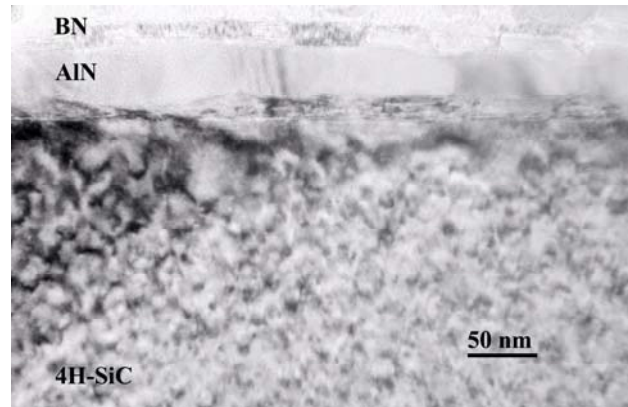

Figure 8: TEM of the BN/AlN capped sample annealed at 1700º shows a sharp boundary between the AlN and SiC and evidence of a nucleation layer in the AlN at the AlN/SiC interface.

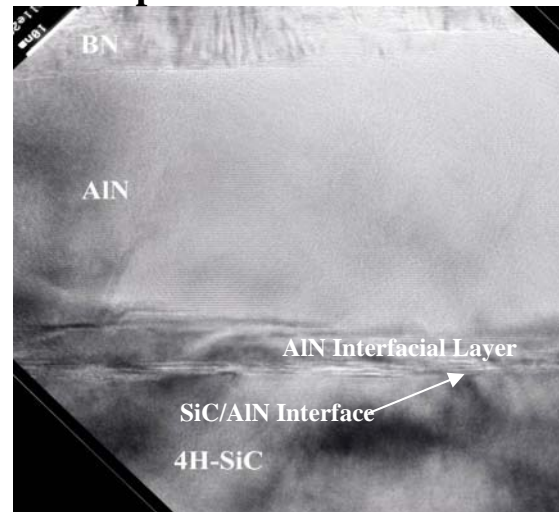### HR TEM of BN/AlN-Capped Sample Annealed at 1700ºC

Figure 9: TEM of the BN/AlN capped sample annealed at 1700º showing the AlN interfacial layer in more detail.

When the C and nitride caps are compared the SEM and AFM micrographs show that at 1800ºC the C-coated sample is smoother, at 1700ºC while at 1650 ºC they are about the same, and at 1600ºC the nitride coated samples are smoother, and at 1500ºC they are about the same.

AFM of SiC Surface with Caps Removed After 1600 or 1800ºC Anneal

C-cap, 1600ºC, 50 x 50 µm   AlN-cap, 1600ºC, 50 x 50 µm

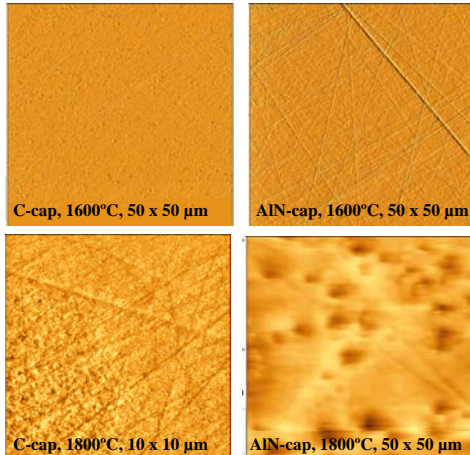C-cap, 1800ºC, 10 x 10 µm   AlN-cap, 1800ºC, 50 x 50 µm

Figure10: Annealed C-capped surfaces contain particulates, increasing with temperature. Annealing had little effect on polishing scratches

The surface of the sample that had been nitride coated and annealed at 1800ºC has a number of hexagonal growth spirals, and the polishing scratches have disappeared. It appears as if surface migration of some of the atoms has occurred. The polishing scratches are still apparent for the C-coated sample annealed at 1800ºC, and the surface has a few pits. The polishing scratches are apparent for both types of caps annealed at 1700ºC, and there are only a few pits in the surface. There is no evidence that growth spirals have formed. The nitride capped samples annealed at the lower temperatures show no signs of deterioration, and do not contain any precipitates on the surface. The C-coated samples annealed at 1600 or 1650ºC, however, have precipitates – possibly reactants from reactions between C and Si - on their surface. This should lead to significantly different behavior in the MOSFETs fabricated from them. It is less clear how this will affect conductivity in the bulk.

SEM of SiC Surface with Caps Removed After 1800ºC Anneal

C-Cap, 500X   C-Cap, 10,00X
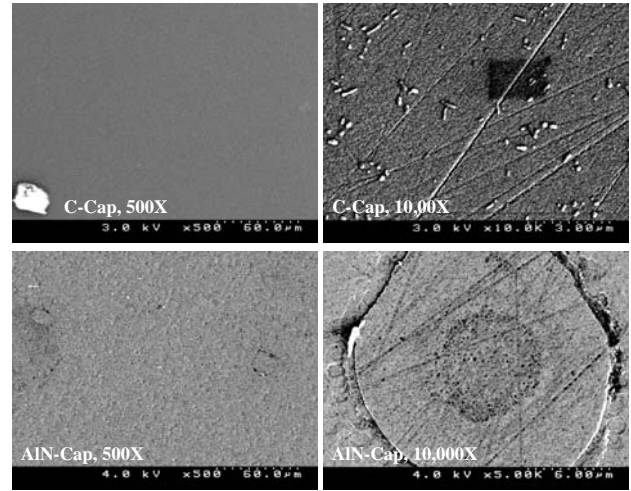
AlN-Cap, 500X   AlN-Cap, 10,000X

Figure 11: C-capped surface contains particulates
C-capped surface at low mag looks good, AlN-capped surface at low mag is rough
Not all of the AlN is removed from the SiC surface
Annealing had little effect on polishing scratches

SEM of SiC Surface with Caps Removed After 1600ºC Anneal

C-Cap, 500X   C-Cap, 10,000X
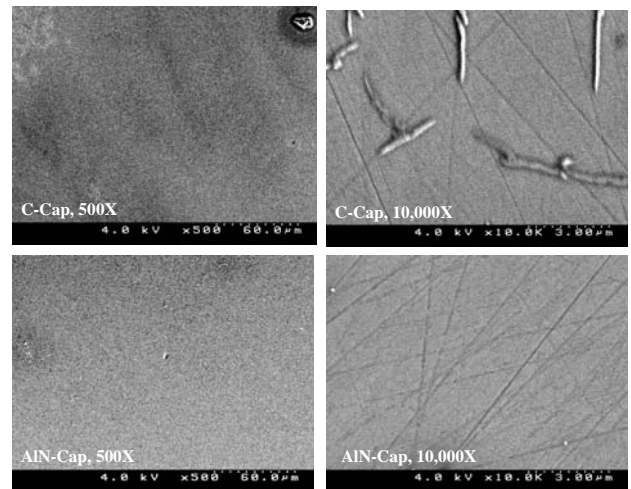
AlN-Cap, 500X   AlN-Cap, 10,000X

Figure 12: C-capped surface contains particulates. Surfaces at low mag look very good. Annealing had little effect on polishing scratches.

AFM of Selected SiC Surface Area with C-Cap Removed After 1650ºC Anneal; SEM of C-cap of another sample
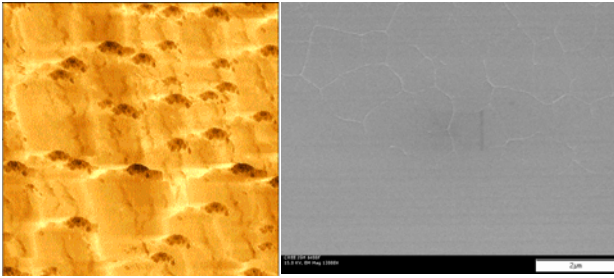

Figure 13: Protuberances outline thermal damage; lines could represent cracks or grain boundaries in the C-cap This type of damage is not found frequently

The type of cap does not appear to affect the sheet resistively. Both types had sheet resistivities of 6×10^4 $\Omega/\square$ after 1600ºC anneal that decreased asymptotically with temperature to 2×10^4 $\Omega/\square$ after 1800ºC anneal. There was little change after the 1650ºC anneal.
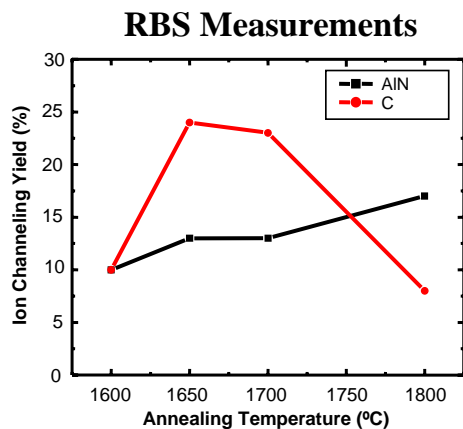
RBS Measurements

Figure 14
Tabulated results form RBS spectra for samples annealed at different temperatures with a nitride or C cap.

The relatively large Rutherford backscattering spectroscopy, RBS χmin is large for all samples and is likely due to polishing damage substrate as the samples are not expitaxial films. There are some trends in the data. For the nitride cap χmin is smallest at the lowest annealing temperature, showing that the samples had the least amount of damage. The increase is likely to be due to the formation of surface particulates and the change in implant damage with increasing temperature. The graphite cap shows conflicting data. The relatively large change at before 1800ºC must be due in part to formation of C granules on the surface.

It is unclear why χmin for the C-capped sample annealed at 1800ºC is relatively small; possibly more

material is removed at 1800ºC by evaporation, but SIMS data confirms that the implant is not substantially affected.

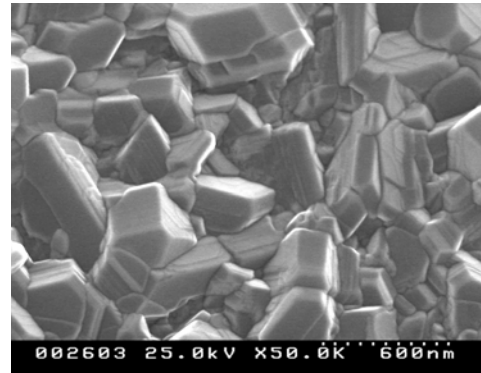**SEM of a Previous C-Cap After A 1700ºC Anneal**

Figure 15: In a previous work we found that the graphite crystallized after a 1700ºC anneal; apparently how the graphite is pretreated affects its ability to crystallize. The infrequent thermal damage observed could have been caused by the beginning of crystallization in selected areas.

CONCLUSIONS

AlN-caps produce better results for annealing temperatures below 1700ºC. C-caps leave particulates on the surface that cannot be removed with a piranha etch. More silicon appears to out-diffuse when a C-cap is used. C-caps produce better results for annealing temperature above 1700ºC. An AlN nucleation layer cannot be completely etched off when it is annealed above 1700ºC. Sample annealed at 1800ºC with a C-cap had the least amount of damage.

When using the easy to prepare C-caps one should be aware that. Graphite can crystallize allowing thermal damage to form at the grain boundaries. Crystallite graphite formed at 1700ºC and above is virtually impossible to etch off. The C-cap has a high evaporation rate when it is annealed at 1800ºC if it hasn't crystallized

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